

**A STUDY OF PARATHION AND PARAOXON RESIDUE
IN CITRUS GROVES FOLLOWING APPLICATION OF PARATHION
AT VARIOUS DOSAGE AND DILUTION RATES**

**Fresno County, May 1975
Orange County, May-June 1975
Tulare County, June-July 1975**

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Poisoning incidents involving field workers who have entered presumably safe parathion-treated citrus groves near or after expiration of an applicable safety interval have spawned interest in the possible mechanism of such unexplained poisonings. In an attempt to learn more about the persistence of parathion residues in citrus groves, foliage and soil samples were collected from several groves following applications of parathion at various dosage and volume rates. The samples were analyzed for dislodgeable and penetrated residues of parathion and its highly toxic degradation product, paraoxon.

METHODS AND MATERIALS

The Applications

The six applications studied were designated plot 1 through 6 for convenience. The application details are given in Table 1.

Sampling Procedure

Leaf punches were used to collect three samples of leaf discs at each sampling interval. Duplicate samples were analyzed for dislodgeable and penetrated residues, total residue values were obtained from the third. The foliage sampling procedure varied in each locality. In plot one each sample consisted of 100 leaf discs, 1.8 cm. in. diameter, taken from separate twenty-five tree groups which were selected and marked throughout the 20 acre grove. Each sample taken from plots 2 and 3 contained 96 leaf discs, 1.8 cm. in. diameter, collected from four locations on each of 12 adjacent trees. On plots 4, 5 and 6 samples were comprised of 40 leaf discs, 2.5 cm. in. diameter, taken from four locations on each of 10 adjacent trees. Sampling locations were at shoulder height in the peripheral foliage and were constant throughout each study. Soil samples were collected with a teaspoon; each sample consisted of 20-1/2 teaspoons of dust and soil scraped to an approximate depth of .5 cm, under the drip line of five trees.

ANALYTICAL PROCEDURES

Extraction

The procedure used in the extraction of dislodgeable, penetrated, and total residues is detailed in an attachment. Total and penetrated residues were extracted with ethyl acetate; dislodgeable residues were partitioned into hexane. Parathion and paraoxon were extracted from soil with Hexane, ethyl ether, and acetone mixed in a 2:1:1 ratio.

Gas Chromatography

The gas chromatographs were Varian models 2100 and 2700 operated under the following conditions:

Varian 2100

Flame photometric detector @ 250°C.

Detector gas flow rates H_2 - 100 ml/min.
 Air - 80 ml/min.

Column - 5.25' x 2 mm I.D. of 3% OV-101 on 100/120 Gas Chrom Q
(carbowax vapor deposition treated) @ 185°C.

Carrier gas - N_2 30 ml/min.

Retention times: Paraoxon - 2.5 minutes
 Parathion - 3.5 minutes

Response ratios: Parathion - 1.0
 Paraoxon - 1.0

Varian 2700

Flame photometric detector @ 250°C.

Detector gas flow rates H_2 - 100 ml/min.
 Air - 80 ml/min.

Column - 6.0' x 2 mm I.D. of 3% OV-10 on 100/120 Gas Chrom Q @
185°C.

Carrier gas - N_2 30 ml/min.

Retention times: Paraoxon - 4 minutes
 Parathion - 5 minutes

Response ratios: Parathion - 0.1
 Paraoxon - 1.0

Quantitation of parathion and paraoxon residues were accomplished by comparison of standard and sample peak heights, which were matched to within $\pm 10\%$.

RESULTS AND DISCUSSION

Daily weather observations made at the study localities are given in Table 2. Dislodgeable, penetrated, and total residue levels are given in Table 3.

The tolerance level for parathion on citrus for human consumption is 1 ppm. The 1 ppm level of combined parathion and paraoxon dislodgeable residue on foliage is considered safe for work involving substantial foliar contact. When parathion is applied as a dilute spray (0.5 lbs./100 gallons) at 4 pounds or less per acre, the combined parathion and

paraoxon level appears to drop below 1 ppm within 15 days after application (Figures 1, 3). Applications of dilute sprays (0.625 lbs/100 gallons) at the higher rates of 7.5 and 10 pounds per acre resulted in the combined parathion-paraoxon dislodgeable residue levels remaining above 1 ppm 30 days after application (Figures 2, 3).

Application of parathion as a concentrate spray at 10 pounds per acre resulted in greatly increased foliar residues which may not reach safe levels until well beyond 30 days (Figure 3). Identical applications of wettable powder and emulsifiable concentrate formulations resulted in similar residue levels (Figure 2). Water washing trees in plot 5 proved effective in reducing dislodgeable residue (Table 3, Figure 3). Parathion residue on dry dust and soil degrades slowly (Figure 4). Paraoxon continued to increase in plot 5 soil at 25 days after application.

The current California reentry safety intervals for parathion applied to citrus are, 21 days when 4 pounds or less actual parathion per acre is applied in a single application; 30 days when 4 to 8 pounds is applied, with no more than 10 lbs. in the last 12 months; 45 days when more than 8 pounds per single application or more than 10 pounds per acre are applied in the last 12 months. These intervals would appear to insure field worker safety in most cases. The margin of safety involved in repeated and heavy applications of parathion may not be large enough to insure complete safety when environmental conditions favor extreme persistence of residues.

TABLE 1

<u>Plot</u>	<u>Location</u>	<u>Date</u>	<u>Applicator</u>	<u>Formulation</u>	<u>Dilution</u>	<u>Gallons Per Acre</u>	<u>Actual Parathion Per Acre (Pounds)</u>
1	Orange Cove (a)	4/27/75	Crumblyss & Horton Pest Con.	Chevron 8EC	1/2 pts. /100 gal.	500 (c)	2.5
2	Woodlake (b)	6/17/75	University of Calif., (Lindcove Field Sta.)	Chevron 8EC	1/2 pts. /100 gal.	1,500 (c)	7.5
3	Woodlake (b)	6/17/75	U.C. Field Station	Dune, 25% Wettable Powder	2 lbs. /100 gal.	1,500 (c)	7.5
4	Tustin (b)	5/24/75	University of Calif., Riverside Personnel	FMC, 25% Wettable Powder	1 lb. /100 gal.	1,600 (d)	4
5	Tustin (b)	5/24/75	UCR Pers.	FMC, 25% Wettable Powder	2.5 lbs. /100 gal.	1,600 (d)	10
6	Tustin (b)		UCR Pers.	FMC, 25% Wettable Powder	40 lbs. /100 gal.	100 (e)	10

- (a) Previous application history unknown.
 (b) No previous parathion applications this season.
 (c) Speed sprayer.
 (d) Oscillating boom sprayer.
 (e) Kinhelder sprayer.

TABLE 2

DAILY TEMPERATURE AND PRECIPITATION OBSERVATIONS
MADE AT THE STUDY PLOT LOCALITIES

ORANGE COVE, FRESNO COUNTY, CALIFORNIA

<u>Date</u>	<u>TEMPERATURE °F</u>		<u>PRECIPITATION</u>	
	<u>24 Hours</u>		<u>24 Hour Amounts</u>	
	<u>Ending at 10:00 A.M.</u>		<u>Observation Time 10:00 A.M.</u>	
	<u>Maximum</u>	<u>Minimum</u>		
4/27	65	37		
4/28	71	43		
4/29	74	43		
4/30	78	48		
5/1	80	44		
5/2	80	46		
5/3	81	43		
5/4	78	44		
5/5	63	35		
5/6	72	44		
5/7	71	44		
5/8	79	46		
5/9	83	49		
5/10	85	49		
5/11	87	47		
	<u>76.4</u>	<u>43.5</u>	<u>Total</u>	<u>0</u>

LEMON COVE, TULARE COUNTY, CALIFORNIA

<u>Date</u>	<u>TEMPERATURE °F</u>		<u>PRECIPITATION</u>	
	<u>24 Hours</u>		<u>24 Hour Amounts</u>	
	<u>Ending at 8:00 A.M.</u>		<u>Observation Time 8:00 A.M.</u>	
	<u>Maximum</u>	<u>Minimum</u>		
6/17	93	56		
6/18	85	55		
6/19	80	50		
6/20	78	55		
6/21	81	61		
6/22	93	61		
6/23	89	56		
6/24	81	50		
6/25	78	42		
6/26	82	50		
6/27	90	56		
6/28	91	50		
6/29	93	53		
6/30	94	53		
7/1	91	50		
7/2	87	50		
7/3	88	52		
7/4	89	52		
7/5	90	54		
7/6	92	54		
7/7	97	59		
7/8	96	60		
7/9	94	65		
7/10	91	62		
7/11	101	61		
7/12	102	60		
7/13	99	59		
7/14	97	62		
7/15	98	58		
7/16	87	62		
	$\bar{x}90.3$	$\bar{x}55.5$	Total	0

TUSTIN, ORANGE COUNTY, CALIFORNIA

<u>Date</u>	<u>TEMPERATURE °F</u>		<u>PRECIPITATION</u>	
	<u>24 Hours</u>		<u>24 Hour Amounts</u>	
	<u>Ending at 3:00 P.M.</u>		<u>Observation Time 3:00 P.M.</u>	
	<u>Maximum</u>	<u>Minimum</u>		
5/24	76	42		
5/25	76	-		
5/26	73	-		
5/27	74	-		
5/28	70	51		
5/29	75	-		
5/30	74	-		
5/31	78	-		
6/1	75	55		
6/2	76	52		
6/3	71	47		
6/4	71	47		
6/5	73	51		
6/6	76	52		
6/7	77	55		
6/8	71	51		
6/9	71	52		
6/10	77	55		
6/11	77	56		
6/12	83	56		
6/13	72	52		
6/14	75	58		
6/15	78	57		
6/16	73	58		
6/17	66	56		
6/18	66	49		
6/19	67	50		
	$\bar{x}73.7$	$\bar{x}52.5$	Total	0

TABLE 3

PARATHION AND PARAOXON RESIDUE FOUND ON
CITRUS FOLIAGE FOLLOWING APPLICATION OF PARATHION
AT VARIOUS DOSAGE AND DILUTION RATES (PPM)

	Time Post Application	Dislodgeable Residue		Penetrated Residue		Total Residue	
		Parathion	Paraoxon	Parathion	Paraoxon	Parathion	Paraoxon
Plot 1 2.5 lbs. /500 gal. /acre	1 day	13.8	.86	33.5	1.9	57.0	3.0
		10.8	.80	24.4	1.5		
	5 days	1.1	0.1	29.5	2.2	25.6	2.4
		1.6	0.1	27.1	2.4		
	9 days	0.56	0.1	21.3	1.6	21.0	1.5
		0.60	0.1	23.4	1.8		
	11 days	0.12	0.1	22.3	1.4	19.1	1.4
		0.07	0.1	16.0	1.3		
	15 days	0.4	N.D.*	13.6	0.7	13.4	0.9
		.5	N.D.	14.3	0.8		
Plot 2 7.5 lbs. /1500 gal. /acre	1 hour	119	1.9	62.6	0.8	191	3.2
		111	1.7	54.6	0.7		
	6 days	2.5	1.1	7.7	1.5	13.8	3.1
		3.2	1.4	6.6	1.4		
	13 days	1.4	0.6	3.8	0.8	2.9	1.3
		1.4	0.4	4.2	0.9		
	21 days	1.8	0.2	3.0	0.8	3.2	0.8
		2.2	0.2	3.0	0.8		
	29 days	0.2	0.5	3.5	0.9	6.1	0.9
Plot 3 7.5 lbs /1500 gal. /acre	1 hour	123	1.7	67.0	1.0	155	2.2
		111	1.9	56.2	1.2		
	6 days	3.0	1.3	4.7	1.0	8.6	4.0
		3.9	1.8	7.3	1.6		
	13 days	1.1	1.0	3.1	1.0	4.5	1.1
		1.3	1.4	2.3	0.7		
	21 days	0.5	0.6	2.5	0.5	3.7	0.9
		0.8	0.4	2.5	0.5		
	29 days	0.2	0.5	2.8	0.7	2.07	0.7

*Not Detectable

	Time Post Application	Dislodgeable Residue		Penetrated Residue		Total Residue	
		Parathion	Paraoxon	Parathion	Paraoxon	Parathion	Paraoxon
Plot 4 4 lbs /1600 gal. /acre	4 days	2.6	0.5	5.4	3.8	10.8	3.1
		10.0	0.7	8.5	3.8		
	10 days	0.5	0.5	4.4	2.1	5.1	2.5
		0.5	0.5	4.3	2.6		
	17 days	.7	N.D.	2.8	0.6	4.6	1.2
		.8	N.D.	2.1	0.6		
	27 days	0.3	N.D.	2.6	0.7	2.4	0.6
		0.5	N.D.	2.4	0.5		
Plot 5 10 lbs. /1600 gal. /acre	4 days	32.1	2.0	47.3	10.2	62.6	9.1
		17.0	1.4	30.4	9.4		
	10 days	5.4	0.5	20.9	8.8	21.8	8.1
		3.6	0.5	15.2	6.5		
	17 days	2.8	N.D.	3.2	0.9	22.8	4.9
		1.6	N.D.	7.2	2.0		
	27 days	6.1	0.5	11.5	1.9	14.6	2.5
		0.9	0.5	10.9	1.8		
Plot 5 (soil)	4 days					82.3	3.5
	10 days					56.1	5.1
	17 days					56.4	5.6
	27 days					35.9	6.8
Plot 5 (washed portion)	4 days	5.7	0.3	30.3	10.3	46.0	8.2
		6.7	0.3	29.9	10.6		
	10 days	0.5	0.5	15.4	6.1	16.9	7.5
		0.7	0.5	14.8	6.0		
	17 days	0.7	N.D.	6.9	2.5	16.4	3.3
		0.9	N.D.	10.1	4.6		
	27 days	0.6	N.D.	8.7	1.9	13.7	3.0
		0.8	N.D.	12.9	2.3		
Plot 6 10 lbs. /100 gal. /acre	4 days	108	4.9	124	22.1	309	19.7
		88.7	5.1	115	18.8		
	10 days	31.1	4.2	64.1	16.1	96.3	21.2
		40.9	5.6	64.1	22.5		
	17 days	7.4	0.4	35.6	3.4	46.1	8.4
		11.4	0.3	41.4	3.6		
	27 days	5.5	1.2	28.9	1.9	12.4	1.1
		2.8	0.8	26.4	2.3		

FIGURE 1

Dislodgeable residue following application of 2 1/2 lbs. active parathion at 500 gallons volume, Fresno County, California, May 1975.

● - parathion
○ - paraoxon

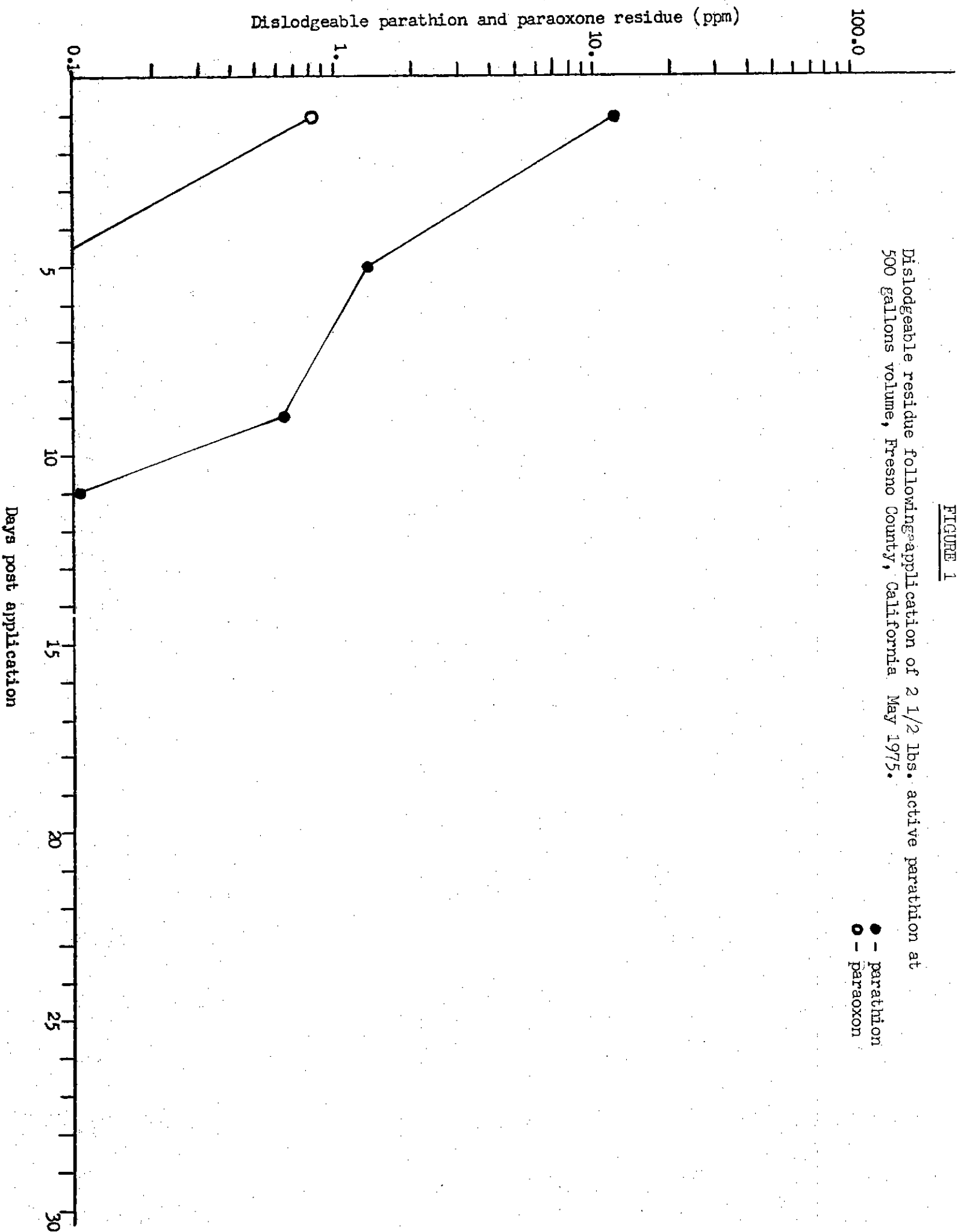


FIGURE 2

Dislodgeable residue following application of emulsifiable concentrate and wettable powder formulations at 7.5 lbs active per acre at 1500 gallons volume, Tulare County California June - July 1975.

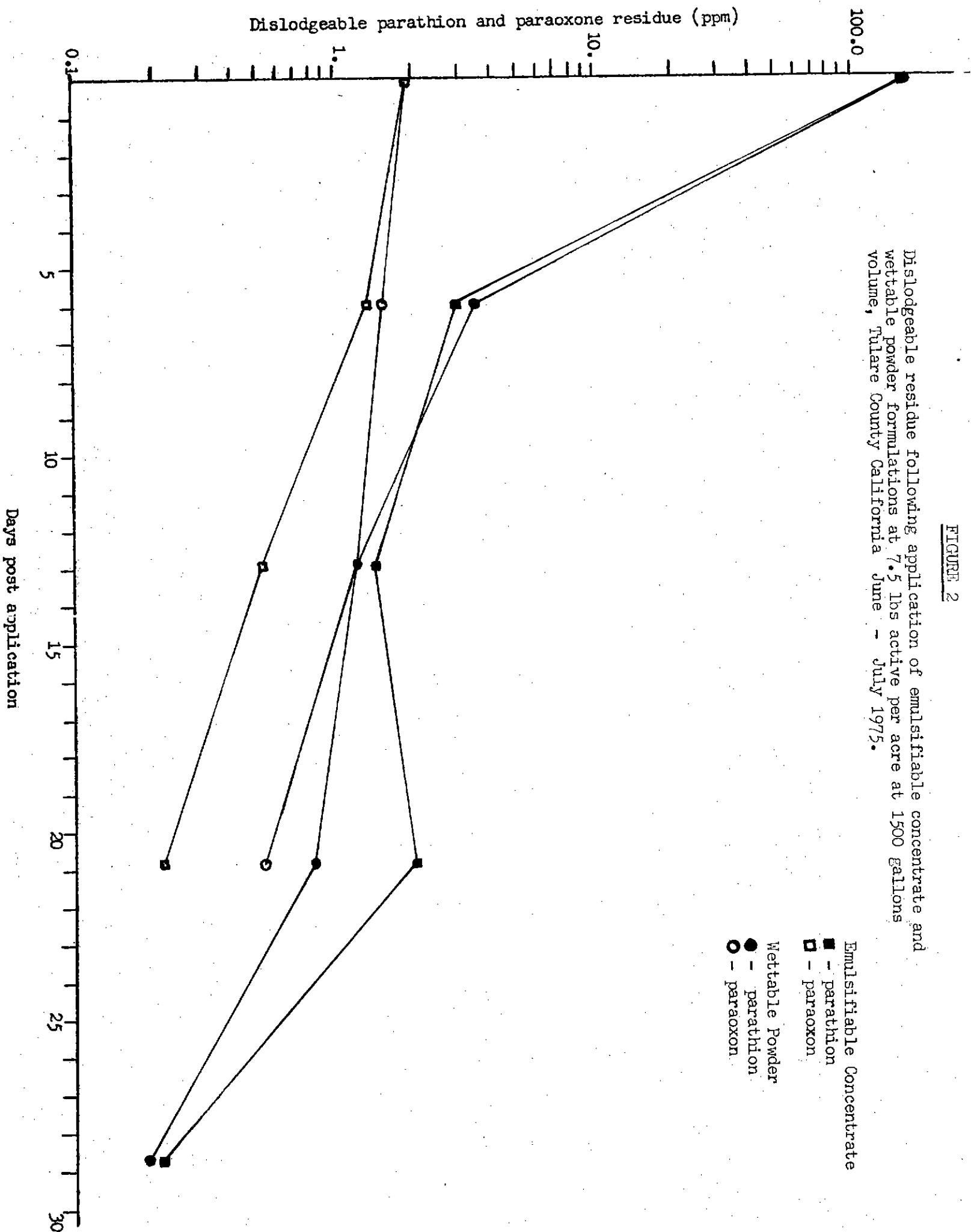


FIGURE 3

Dislodgeable residue following applications of parathion 25% wettable powder at various dosages and volume, Orange County California May - June 1975.

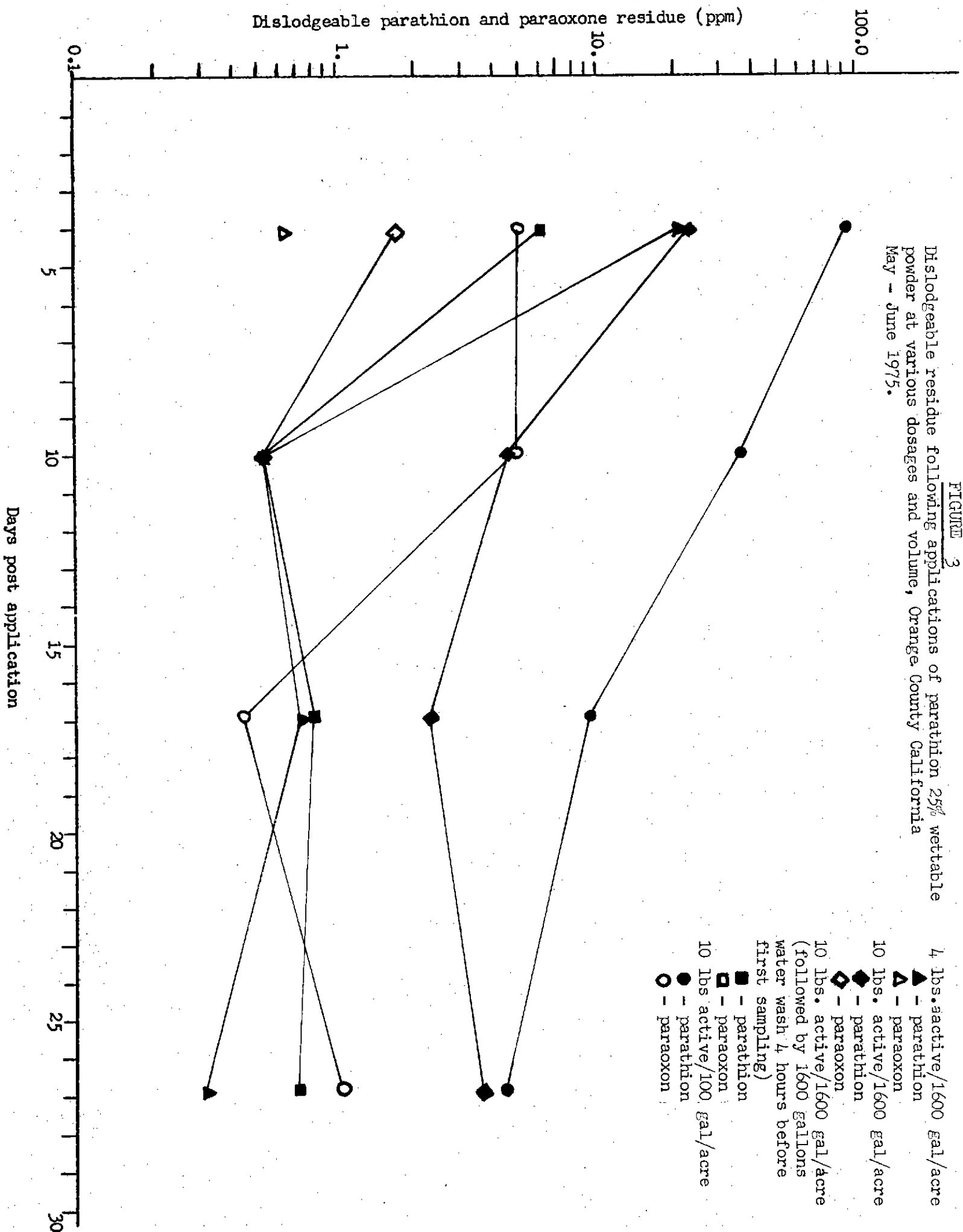


FIGURE 4
Residue found in soil beneath trees following application of parathion 25% wettable powder 10 lbs. active per acre at 1600 gallons volume, Orange County, California
May - June 1975.

